



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 126 539 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
22.08.2001 Bulletin 2001/34

(51) Int Cl. 7: H01M 16/00

(21) Application number: 01301379.2

(22) Date of filing: 16.02.2001

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR  
Designated Extension States:  
AL LT LV MK RO SI

(72) Inventors:  
• Gan, Hong  
East Amherst, New York 14051 (US)  
• Takeuchi, Esther S.  
East Amherst, New York 14051 (US)

(30) Priority: 16.02.2000 US 183010 P

(74) Representative: Bradley, Josephine Mary et al  
Mathys & Squire  
100 Gray's Inn Road  
London WC1X 8AL (GB)

(71) Applicant: WILSON GREATBATCH LTD.  
Clarence New York 14031 (US)

## (54) Electrochemical battery for conversion of low rate energy into high rate energy by parallel discharging

(57) An electrode configuration for use in a defibrillator battery to improve the battery capacity and its utilization efficiency by using a combination SVO cell and a CF<sub>x</sub> cell discharged in parallel, is described. In other words, the anode of the SVO cell is connected to the

anode of the CF<sub>x</sub> cell and the cathode of the SVO cell is connected to the cathode of the CF<sub>x</sub> cell. The SVO cell provides a relatively high discharge rate while the CF<sub>x</sub> cell results in long service life. This results in 100% of the usable capacity from both cells being utilized.

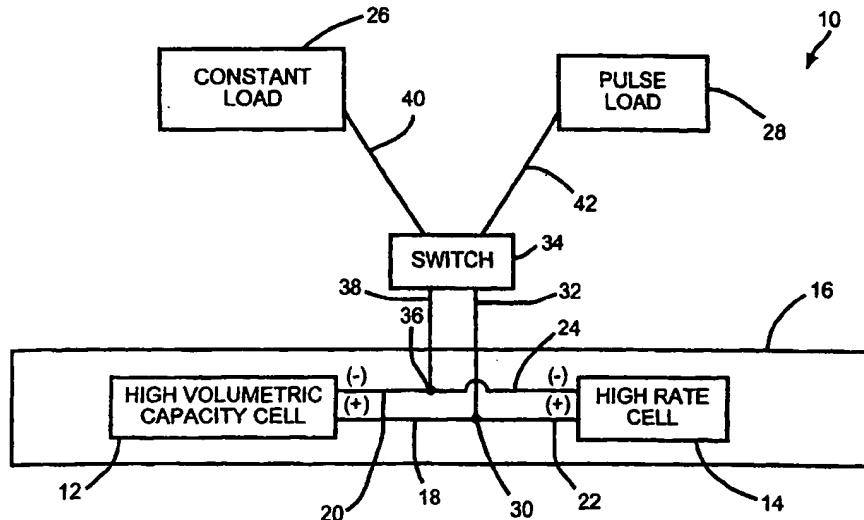


FIG.1

EP 1 126 539 A2

**Description****CROSS REFERENCE TO RELATED APPLICATION**

5 [0001] The present application claims priority based on provisional application Serial No. 60/183,010, filed February 16, 2000.

**BACKGROUND OF THE INVENTION**10 **1. Field Of Invention**

[0002] The present invention generally relates to the conversion of chemical energy to electrical energy. More particularly, the present invention relates to a high capacity lithium electrochemical cell designed for high rate discharge applications, such as are required to power a cardiac defibrillator.

15 **2. Prior Art**

20 [0003] Early ventricular cardiac defibrillators used two lithium batteries, in series, as their power source. Due to the progress of new circuit designs, the electronic circuit in a defibrillator now consumes less energy than required by earlier models. This makes it possible for the present generation of defibrillators to be powered by a single lithium electrochemical cell. With a one cell design, the requirement for high current pulse capability, or power density, is even greater due to the lowered pulsing voltage. Large electrode surface area is thus needed to accomplish this requirement. In general, when a cell's electrode surface area is increased, more inert materials (current collector, separator, etc.) are incorporated into the casing. As a result, the cell volumetric capacity is decreased. One of the concerns in such a design is the longevity of the medical device, which is dependent on the cell's capacity and power efficiency.

25 [0004] The capacity of an electrochemical cell is not only dependent on the electrode design and packing efficiency, it is also dependent on the type of electrode active materials used. For example, for silver vanadium oxide (SVO) cells, the e-phase having the formula  $\text{AgV}_2\text{O}_{5.5}$  is preferred as the cathode active material. Its theoretical volumetric capacity is determined to be 1.37 Ah/ml. By comparison, the theoretical volumetric capacity of fluorinated carbon ( $\text{CF}_x$ ) cathode active material ( $x = 1.1$ ) is 2.42 Ah/ml, which is 1.77 times greater than the theoretical capacity of SVO. However, in cardiac defibrillator applications, SVO is preferred because it can deliver relatively high current pulses or high energy within a short period of time. Although the  $\text{CF}_x$  active material has higher volumetric capacity, it cannot be used in such applications due to its relatively low to medium rate of discharge capability.

30 [0005] Attempts to use high capacity materials, such as  $\text{CF}_x$ , by mixing them with a high rate cathode material, such as SVO are described in U.S. Patent No. 5,180,642 to Weiss et al. Batteries made from such cathode composites exhibit a relatively lower rate capability in comparison to those having SVO as the sole cathode active material. The benefit of increasing the cell's theoretical capacity by using  $\text{CF}_x$  as part of the cathode mix is, in part, canceled by the lowering of this material's relatively high power capability during high rate discharge applications.

35 [0006] Another approach to improving the longevity of cardiac defibrillators powered by cells housed in a single casing is reported in U.S. Patent No. 5,614,331 to Takeuchi et al. This patent describes a method of using a medium rate cell to power the circuitry of the implantable defibrillator and, separately, an SVO cell as the power supply for the device under high rate applications. The cells are described as being housed within a single casing and activated by the same electrolyte. The advantage of this method is that all of the relatively high power of the SVO cell is reserved

40 for high power pulse discharge applications while the low power requirements of monitoring the heart beat and the like are provided by a relatively high capacity active material, such as  $\text{CF}_x$ . However, this method requires a very careful design to balance the capacities of the high power SVO cell with the low power  $\text{CF}_x$  cell to ensure that both reach end situations in device usage by patients.

45 **50 SUMMARY OF THE INVENTION**

50 [0007] The present invention provides for improved discharge performance of lithium electrochemical cells through a new design and a new method of cell discharge. The present invention also provides a new design in defibrillator batteries to improve battery capacity and utilization efficiency, and at the same time to maintain the high current pulse discharge capability throughout service life of the battery. These objectives are achieved by discharging an SVO cell connected in parallel with a  $\text{CF}_x$  cell.

55 [0008] Accordingly, an SVO cell for providing high power capability and a  $\text{CF}_x$  cell for providing high volumetric capacity are connected together in parallel. The anode of the SVO cell is connected to the anode of the  $\text{CF}_x$  cell and

the cathode of the SVO cell is connected to the cathode of the  $\text{CF}_x$  cell. The cells are hermetically housed in a single casing activated with the same electrolyte or hermetically housed in separate cases. The present cell configuration is particularly useful in high rate discharge applications, such as required by cardiac defibrillators. In particular, the SVO cell provides high rate discharge while the  $\text{CF}_x$  cell is useful to achieve long service life. Furthermore, end of service  
 5 life indication during parallel discharge of this novel cell configuration is the same as that of the SVO cell. In other words, both cells reach end of life at the same time in spite of varied usage in actual defibrillator applications. Since both cells reach end of service life at the same time, no discharge energy is wasted and there is no need to balance the capacities of both cells.

[0009] At beginning of life, a typical SVO cell has an under load voltage of around 3.2V. In comparison, a typical  $\text{CF}_x$   
 10 cell has an under load voltage of around 2.8V. According to the present invention, conservation of the high power energy of the SVO cell and the low power energy of the  $\text{CF}_x$  cell in an implantable cardioverter defibrillator application is achieved by discharging the two cells separately until both reach the same voltage. Then, both cells are discharged in parallel.

[0010] These and other aspects of the present invention will become more apparent to those skilled in the art by  
 15 reference to the following description and to the appended drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Fig. 1 is a schematic of a discharge configuration of the combination battery of the present invention.  
 20 [0012] Fig. 2 is an elevational view, partly in schematic of the combination battery shown in Fig. 1.  
 [0013] Fig. 3 is a graph constructed from the pulse discharge of a Li/SVO cell.  
 [0014] Fig. 4 is a graph constructed from the pulse discharge of a Li/SVO connected in parallel with a Li/ $\text{CF}_x$  cell.  
 [0015] Fig. 5 is a graph constructed from the pulse discharge of a single Li/SVO cell in comparison to the pulse  
 25 discharge of a Li/SVO cell connected in parallel with a Li/ $\text{CF}_x$  cell.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] As used herein, the term "pulse" means a short burst of electrical current of a significantly greater amplitude than that of a prepulse current immediately prior to the pulse. A pulse train consists of at least two pulses of electrical  
 30 current delivered in relatively short succession with or without open circuit rest between the pulses. A typical pulse discharge is about 15.0 mA/cm<sup>2</sup> to about 30.0 mA/cm<sup>2</sup>.

[0017] As used herein, the definition of  $\text{CF}_x$  having a relatively high energy density but a relatively low rate capability and SVO having a relatively low energy density but a relatively high rate capability means that SVO is capable of being pulse discharged at about 15.0 mA/cm<sup>2</sup> to about 30.0 mA/cm<sup>2</sup> without its voltage falling below 1.5V. On the other hand,  
 35 if  $\text{CF}_x$  were to be pulse discharged under these conditions, its delivered voltage would fall below 1.5V. The pulse discharge parameter is per cathode surface area.

[0018] Referring now to the drawings, Fig. 1 shows a schematic embodiment of a combination battery 10 constructed according to the present invention having both a high volumetric capacity cell 12 and a high rate cell 14 hermetically sealed in a metallic, prismatic casing 16. Both electrode assemblies are insulated from one another and activated with  
 40 the same electrolyte.

[0019] As shown in Fig. 1, the high volumetric capacity cell 12 has positive and negative electrode terminals 18, 20 while the high rate cell 14 also has its own positive and negative electrode terminals 22, 24. Two different loads are applied to this battery. A constant resistance load 26 and a constant current pulse "load" 28. A device providing both a constant resistant load and a constant current pulse "load" is, for example, an implantable medical device such as  
 45 a cardiac defibrillator. An implantable cardiac defibrillator is a device that requires a power source for a generally medium rate, constant resistance load component provided by circuits performing such functions as, for example, the heart sensing and pacing functions. From time to time, the cardiac defibrillator may require a generally high rate, pulse discharge load component that occurs, for example, during charging of a capacitor in the defibrillator for the purpose of delivering an electrical shock to the heart to treat tachyarrhythmias, the irregular, rapid heartbeats that can be fatal  
 50 if left uncorrected. Reduction and even elimination of voltage delay during a current pulse application is important for proper device operation and extended device life.

[0020] An important aspect of the present invention is that the positive terminal 18 of the high volumetric capacity cell 12 is connected to the positive terminal 22 of the high rate cell 14 at node 30. From there, a common lead 32 connects to a switch 34. Similarly, the negative terminal 20 of the high volumetric capacity cell 12 is connected to the negative terminal 24 of the high rate cell 14 at node 36. A common lead 38 connects between node 36 and switch 34.

[0021] The switch 34 serves to direct the electrical power generated by the combination battery 10 to either the constant power load 26 via connection 40 or to the pulse load requirement via connection 42. For example, in a cardiac defibrillator, the medical device requires a relatively low level current for the maintenance of electronic monitoring

circuits interrupted from time to time by high level current during device activation.

[0022] The anode electrode for both the high volumetric capacity cell 12 and for the high rate cell 14 is selected from Group IA of the Periodic Table of Elements, including lithium, sodium, potassium, etc., and their alloys and intermetallic compounds including, for example Li-Si, Li-B and Li-Si-B alloys and intermetallic compounds. The preferred anode comprises lithium, and the more preferred anode comprises a lithium alloy, the preferred lithium alloy being lithium-aluminum with the aluminum comprising from between about 0% to about 50%, by weight, of the alloy. The greater the amount of aluminum present by weight in the alloy the lower the energy density of the cell.

[0023] The anode for both the high volumetric capacity cell 12 and the high rate cell 14 is a thin metal sheet or foil of the anode metal, pressed or rolled on a metallic anode current collector, i.e., preferably comprising nickel, to form the respective anode components. As more clearly shown in Fig. 2, the respective anode components 44, 46 for both the high volumetric capacity and high rate cells 12, 14 each have an extended tab or lead 48, 50 of the same material as the anode current collector (not shown), i.e., preferably nickel, integrally formed therewith, such as by welding. The leads 48, 50 extending from the current collector of the anode components for both the high volumetric capacity cell 12 and the high rate cell 14 are contacted by a weld to the conductive metal battery casing 16 in a case-negative configuration for both cells. The battery casing 16 is preferably a prismatic housing that may comprise materials such as stainless steel, mild steel, nickel-plated mild steel, titanium or aluminum, but not limited thereto, so long as the metallic material is compatible for use with components of the cells.

[0024] Another important aspect of the present invention is that the cathode active material of the high volumetric capacity cell 12 is of any chemistry having a greater volumetric capacity than the cathode active material of the high rate cell 14. In that regard, the cathode active material of the high rate cell 14 is of any chemistry having a higher power capacity than that of the other cell 12.

[0025] Preferably, the cathode active material for the high volumetric capacity cell 12 comprises a solid active material such as fluorinated carbon represented by the formula  $(CF_x)_n$ , wherein x varies between about 0.1 to 1.9 and preferably between about 0.5 and 1.2 and  $(C_2F)_n$ , and wherein the n refers to the number of monomer units which can vary widely. These electrode active materials are composed of carbon and fluorine, and include graphitic and non-graphitic forms of carbon, such as coke, charcoal or activated carbon. Other cathode active materials include  $Ag_2O$ ,  $Ag_2O_2$ ,  $CuF_2$ ,  $Ag_2CrO_4$  SVO and  $MnO_2$ .

[0026] Before fabrication into a cathode electrode for incorporation into the cell 12, the fluorinated carbon active material is preferably mixed with a conductive additive. Suitable conductive additives include acetylene black, carbon black and/or graphite. Metals such as nickel, aluminum, titanium and stainless steel in powder form are also useful as conductive diluents when mixed with the above listed active materials. The electrode further comprises a binder material which is preferably a fluoro-resin powder such as powdered polytetrafluoroethylene (PTFE) or powdered polyvinylidene fluoride (PVDF). The preferred cathode active mixture comprises  $CF_x$  combined with acetylene black and/or graphite; and PTFE. This active mixture in a dry powder form is pressed onto a conductive metal screen. Suitable materials for the cathode current collector include aluminum and titanium, preferably titanium. In some cases, the cathode electrode mentioned above onto a suitable current collector.

[0027] The cathode electrode for the high volumetric cell 12, prepared as described above, is preferably in the form on one or more structures such as one or more cathode plates 52 operatively associated with at least one or more anode structures such as anode plate 44 of the previously described anode material. Preferably, at least one cathode plate 52 is flanked on either side by oppositely positioned anode plates 44.

[0028] The cathode electrode for the high rate cell 14 may comprise a metal element, a metal oxide, a mixed metal oxide, a metal sulfide or carbonaceous compounds, and combinations thereof. Suitable cathode active materials include silver vanadium oxide,  $V_2O_5$ , copper vanadium oxide, copper silver vanadium oxide (CSVO), manganese dioxide, titanium disulfide, copper oxide, copper sulfide, iron sulfide, iron disulfide, vanadium pentoxide, lithium cobalt oxide, lithium nickel oxide, lithium manganese oxide and mixtures thereof.

[0029] Preferably, the cathode active material for the high rate cell 14 comprises a mixed metal oxide formed by a chemical addition, reaction or otherwise intimate contact or by a thermal spray coating process of various metal sulfides, metal oxides or metal oxide/elemental metal combinations. The materials thereby produced contain metals and oxides of Groups IB, IIB, IIIB, IVB, VB, VIB, VIIIB and VIII of the Periodic Table of Elements, which includes the noble metals and/or their oxide compounds.

[0030] By way of illustration, and in no way intended to be limiting, an exemplary cathode active material for the high rate cell 14 comprises silver vanadium oxide having the general formula  $Ag_xV_2O_y$  in any one of its many phases, i.e.,  $\beta$ -phase silver vanadium oxide having in the general formula  $x = 0.35$  and  $y = 5.18$ ; Y-phase silver vanadium oxide having in the general formula  $x = 0.80$  and  $y = 5.40$  and  $\epsilon$ -phase silver vanadium oxide having in the general formula  $x = 1.0$  and  $y = 5.5$ , and combination and mixtures of phase thereof.

[0031] As shown in Fig. 2, the high rate cell 14 of the combination battery 10 preferably has the cathode electrode in the form of a strip 54 wound with a corresponding strip of anode material in a structure similar to a "jellyroll". For

that purpose, the cathode electrode 54 is in the form of a free-standing sheet of cathode material that has been cal-  
 endared from a paste including binder and conductive additives, dried and cut to shape. The shaped cathode plate is  
 then pressed onto at least one side and preferably both sides of a current collector screen of a suitable material such  
 as aluminum or titanium, aluminum being preferred. A process for making cathode components useful in the high rate  
 5 cell of the present combination battery is described in U.S. Patent No. 5,435,874 to Takeuchi et al., which is assigned  
 to the assignee of the present invention and incorporated herein by reference.

[0032] As shown in Fig. 2, the lead 18 for the cathode plates 52 of the high volumetric capacity cell 12 and the leads  
 10 22 for the cathode strip 54 of the high rate cell 14 are insulated from the casing 16 such as by respective glass-to-  
 metal seal/terminal pin feedthroughs 56, 58. The glass used is of a corrosion resistant type having from between about  
 0% to about 50% by weight silicon such as CABAL 12, TA 23, FUSITE 425 or FUSITE 435. The positive terminal pin  
 feedthroughs preferably comprise molybdenum although titanium, aluminum, nickel alloy, or stainless steel can also  
 be used.

[0033] While the present invention is described having the anode leads 48, 50 connected to the casing 16 and the  
 15 cathode leads 18, 22 insulated from the casing, the combination battery 10 can also be constructed in a case-positive  
 configuration. This requires connecting the cathode leads 18, 22 to the casing 16 insulated from the anode terminals.

[0034] The anode components 44, 46 and the cathode structures 52, 54 for the respective high volumetric capacity  
 20 and high rate cells 12, 14 are preferably sealed in their own separator envelopes (not shown for clarity) to prevent  
 direct physical contact between the operatively associated anode electrodes and the cathode electrodes. In the case  
 of the high volumetric capacity cell 12, an insulative bag 60 (shown in dashed lines in Fig. 2) is provided to surround  
 the operatively associated cathode electrode and anode electrode to prevent direct contact between the high volumetric  
 capacity and high rate cells. The insulative bag 60 is of a similar material as the separators.

[0035] The separators for both cells are of electrically insulative material to prevent an internal electrical short circuit  
 25 between the electrodes, and the separator material also is chemically unreactive with the anode and cathode active  
 materials and both chemically unreactive with and insoluble in the electrolyte. In addition, the separator material has  
 a degree of porosity sufficient to allow flow therethrough of the electrolyte during the electrochemical reaction of the  
 30 respective cells. Illustrative separator materials include fabrics woven from fluoropolymeric fibers including polyvinylidene  
 fluoride, polyethylenetetrafluoroethylene, and polyethylenchlorotrifluoroethylene laminated with a fluoropolymer-  
 ic microporous film, non-woven glass, polypropylene, polyethylene, glass fiber material, ceramics, polytetrafluoroeth-  
 35 ylene membrane commercially available under the designation ZITEX (Chemplast Inc.), polypropylene membrane,  
 commercially available under the designation CELGARD (Celanese Plastic Company, Inc.) and a membrane com-  
 mercially available under the designation DEXIGLAS (C. H. Dexter, Div., Dexter Corp.).

[0036] The combination electrochemical battery of the present invention further includes a nonaqueous, ionically  
 40 conductive electrolyte which serves as a medium for migration of ions between the anode and the cathode electrodes  
 during the electrochemical reactions of both the high volumetric capacity and the high rate cells. The electrochemical  
 45 reaction at the electrodes involves conversion of ions in atomic or molecular forms which migrate from the anode to  
 the cathode. Thus, nonaqueous electrolytes suitable for the present invention are substantially inert to the anode and  
 cathode materials, and they exhibit those physical properties necessary for ionic transfer namely, low viscosity, low  
 50 surface tension and wettability.

[0037] A suitable electrolyte for both cells has an inorganic, ionically conductive salt dissolved in a nonaqueous  
 solvent, and more preferably, the electrolyte includes an ionizable alkali metal salt dissolved in a mixture of aprotic  
 55 organic solvents comprising a low viscosity solvent and a high permittivity solvent. Preferably, the ion-forming alkali  
 metal salt is similar to the alkali metal comprising the anode. Suitable salts include LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiAsF<sub>6</sub>, LiSbF<sub>6</sub>, LiClO<sub>4</sub>,  
 LiAlCl<sub>4</sub>, LiGaCl<sub>4</sub>, LiC(SO<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>, LiO<sub>2</sub>, LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>, LiSCN, LiO<sub>3</sub>SCF<sub>2</sub>CF<sub>3</sub>, LiC<sub>6</sub>F<sub>5</sub>SO<sub>3</sub>, LiO<sub>2</sub>CCF<sub>3</sub>, LiSO<sub>3</sub>F, LiB  
 (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, and mixtures thereof. Suitable salt concentrations typically range between about 0.8 to 1.5 molar.

[0038] Low viscosity solvents include esters, linear and cyclic ethers and dialkyl carbonates such as tetrahydrofuran  
 (THF), methyl acetate (MA), diglyme, triglyme, tetraglyme, dimethyl carbonate (DMC), 1,2-dimethoxyethane (DME),  
 diisopropylether, 1,2-diethoxyethane (DEE), 1-ethoxy,2-methoxyethane, diethyl carbonate, dipropyl carbonate, ethyl  
 60 methyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, and mixtures thereof, and high permittivity solvents  
 include cyclic carbonates, cyclic esters and cyclic amides such as propylene carbonate (PC), ethylene carbonate (EC),  
 butylene carbonate, acetonitrile, dimethyl sulfoxide, dimethyl formalize, dimethyl acetamide, Y-valerolactone, Y-butyl-  
 rolacetone (GBL), N-methyl-pyrrolidinone (NMP) and mixtures thereof. In the present invention, the preferred electro-  
 lyte for the high volumetric capacity cell 12 being of a Li/CF<sub>x</sub> couple is 1.0M to 1.4M LiBF<sub>4</sub> in GBL. The preferred  
 electrolyte for the high rate cell 14 being of a Li/SVO couple is 1.0M to 1.4M LiAsF<sub>6</sub> dissolved in a 50/50 mixture (by  
 volume) of PC and DME.

[0039] The casing header comprises a metallic lid (not shown) having a sufficient number of openings to accommo-  
 date the glass-to-metal seal/terminal pin feedthroughs 56, 58 for the cathode electrodes of the high volumetric capacity  
 and the high rate cells. An additional opening 62 is provided for electrolyte filling. The casing header comprises elements  
 having compatibility with the other components of the electrochemical cells and is resistant to corrosion. The battery

is thereafter filled with the electrolyte solution described hereinabove and hermetically sealed such as by close-welding a stainless steel plug over the fill hole 62, but not limited thereto.

[0040] It is believed that throughout the discharge life of the cells 12, 14, all the pulse discharge energies are provided by the SVO cell. Above 2.9V, the  $\text{CF}_x$  cell does not discharge. Instead, the SVO cell provides all of the discharge energies including those required for pulse discharging as well as for background monitoring. At this stage, the  $\text{CF}_x$  cell is polarized to the SVO cell. Once the cells are discharged to the working voltage of the  $\text{CF}_x$  cell (2.9V or below), both the SVO cell and the  $\text{CF}_x$  cell provide energy for background load discharging. However, only the SVO cell provides energy for high rate pulsing discharge. After the SVO cell is pulse discharged, the potential of the SVO cell tends to drop due to loss of capacity. When the background voltage of the SVO cell drops below the working voltage of the  $\text{CF}_x$  cell, the SVO cell is charged by the parallel connected  $\text{CF}_x$  cell to bring both cells' background voltages to a equal value. Therefore, in practice, the SVO cell acts as a rechargeable cell and at the same time the  $\text{CF}_x$  cell acted as a charger. As a result, both cells reach end of service life at the same time.

[0041] Accordingly, the high volumetric capacity cell 12 connected in parallel with the high rate cell 14 provides the battery dischargeable to deliver a relatively low electrical current on the order of about 1 microampere to about 100 milliamperes for the constant load 26 requirement. At such time as electrical energy is needed for the pulse load 28 requirement, the high rate cell 14 provides electrical current on the order of about 1 amp to about 4 amps.

[0042] It should be pointed out that the high volumetric capacity cell 12 and the high rate cell 14 of the present combination battery 10 can be housed in their own casings. In this case, they are each activated by the electrolytes described above. In another embodiment of the present invention, the cells 12, 14 reside in a single casing and are preferably activated with an electrolyte comprising  $\text{LiAsF}_6$  in DME/PC.

[0043] The following examples describe the manner and process of a combination battery according to the present invention, and they set forth the best mode contemplated by the inventors of carrying out the invention, but they are not to be construed as limiting.

## 25 EXAMPLE I

[0044] Fifteen Li/SVO cells were constructed in the following manner. Lithium anode material was pressed on a nickel current collector screen and silver vanadium oxide cathode material was pressed on a titanium current collector screen. A prismatic cell stack assembly configuration with two layers of microporous membrane polypropylene separator sandwiched between the anode and cathode was prepared. The electrode assembly was then hermetically sealed in a stainless steel casing in a case negative configuration after having been activated with an electrolyte of 1.0M  $\text{LiAsF}_6$  in a 1:1 volume ratio of PC and DME. The theoretical capacity Li/SVO cells built in this manner is 2345 mAh.

[0045] Nine Li/ $\text{CF}_x$  cells were built in the following manner. Lithium anode material was pressed on a titanium current collector screen and  $\text{CF}_x$  cathode material was pressed on a titanium current collector screen. A prismatic cell stack assembly configuration with two layers of polypropylene separator sandwiched between the anode and cathode was prepared. The electrode assembly was then hermetically sealed in a titanium casing in a case negative configuration after having been activated with an electrolyte of 1.0M  $\text{LiBF}_4$  in GBL. The theoretical capacity of the Li/ $\text{CF}_x$  cells built in this manner is 1315 mAh.

[0046] Before the parallel discharge test, 15 SVO cells were predischarged to remove about 644 mAh of capacity. Then, six of the cells were discharged under a 17.4 k $\Omega$  load interrupted by pulse trains applied twice a week. The pulse trains consisted of four 10 second 2.0 Amp pulses with a 15 second rest between each pulse. All six cells were discharged in this manner to end of life, and exhibited with very similar and characteristic SVO cell behavior. The average discharge capacity to various voltage cut offs are summarized in Fig. 3 and below in Table 1. In Fig. 3, curve 70 was constructed from the background voltage of a representative one of the Li/SVO cells, curve 72 is of the pulse 1 minimum (P1 min.) and curve 74 is of the pulse 4 minima (P4 min.) It should be pointed out that the total capacity values set forth in Table 1 were derived by adding the 644 mAh of predischarge capacity plus the capacity read from the p4 min. curve 74 of Fig. 3 to the various voltage cut-offs.

[0047] The remaining nine SVO cells were connected in parallel with the  $\text{CF}_x$  cells to provide nine battery assemblies according to the present invention. As before, these battery assemblies were discharged under a 17.4 k $\Omega$  load interrupted by pulse trains applied twice a week. Similar results were observed for all nine battery assemblies. Interestingly, in addition to the 2.5V to 2.6V voltage plateau typically observed for an SVO cell, another voltage plateau at around 2.8V was observed. The average discharge results for the nine SVO/ $\text{CF}_x$  cell assemblies are summarized in Fig. 4 and in Table 1. In Fig. 4, curve 80 was constructed from the background voltage of the parallel discharged Li/SVO and Li/ $\text{CF}_x$  cells, curve 82 is of the P1 min. of these cells and curve 84 is of the P4 min. As with Fig. 3, the total capacity values set forth in Table 1 were derived from by adding the 644 mAh of predischarge capacity to the capacity read from the p4 min. curve 84 to the various voltage cut-offs.

Table 1

Cell	Total	Capacity at Voltage Cut Off (mAh)					
		2.0V	DOD	1.7V	DOD	1.5V	DOD
SVO	1469	62.6%	1659	70.7%	1754	74.8%	
SVO/CF <sub>x</sub>	2554	69.8%	2824	77.2%	2894	79.1%	
ΔCapacity	1085		1165		1140		

5 [0048] From Table 1 and Figs. 3 and 4, it can be seen that at each voltage cut off, the parallel discharged cell assemblies delivered higher total capacities with significantly higher total discharge efficiencies than the individual SVO cells. The cell background voltages were about 2.51V at a 2.0V cut off, about 2.41V at a 1.7V cut off and about 2.35V at a 1.5V cut off. At these background voltages, a single CF<sub>x</sub> cell typically delivers discharge capacities of about 1148 mAh (2.51V), about 1152mAh (2.41V) and about 1170 mAh (2.35V), respectively under a 16.5 kΩ load. Thus, in the above example, almost 100% of the CF<sub>x</sub> deliverable capacity was converted into high power SVO energy.

10 EXAMPLE II

20 [0049] Two SVO cells and one CF<sub>x</sub> cell were constructed in a similar manner as those described in Example I. One of the SVO cells was discharged under a 9.53 kΩ load interrupted by pulse trains applied every 39 days. The other SVO cell was parallel connected to a CF<sub>x</sub> cell according to the present invention. The resulting cell pack was then discharged under a 9.53 kΩ load interrupted every 39 days by pulse trains. In both cases, the pulse trains were similar to those described above. The results are summarized as a capacity vs. potential plot in Fig. 5. In this graph, curve 90 was constructed from the prepulse of the Li/SVO cell, curve 92 from the pulse 1 min. and curve 94 from the pulse 4 min. In contrast, curve 96 was constructed from the prepulse of the Li/SVO/CF<sub>x</sub> cell, curve 98 from the pulse 1 min. and curve 100 from the pulse 4 min. of this present invention cell.

25 [0050] In the initial three pulse trains, both tests presented similar cell behavior. The background voltages and pulse minimum voltages were almost identical and were typical of SVO cell behavior. After pulse train 3, however, the single SVO cell background voltage dropped to the 2.5V to 2.6V voltage plateau at pulse trains 4, 5 and 6. For the combination SVO/CF<sub>x</sub> cells, the background voltages were maintained at the 2.8V to 2.9V voltage plateau, which is the typical discharge voltage of a CF<sub>x</sub> cell. At pulse train 7, the background voltage of the single SVO cell dropped to 2.35V while the combination cells maintained their background voltage at 2.72V. In addition, the pulse minimum potentials of the parallel SVO/CF<sub>x</sub> cells was still 2.26V, which is substantially higher than that of the single SVO cell at 1.54V.

30 [0051] The single SVO cell reached end of life (EOL) by pulse train 8 while the parallel SVO/CF<sub>x</sub> cells did not reach EOL until pulse train 12. By comparing the cell delivered capacity at EOL for the above two tests, the capacity difference was determined to be about 1,188 mAh, which is consistent with the results obtained in Example I. This added discharge capacity is attributed to the CF<sub>x</sub> cell. These results indicated that during a long term discharge test of the SVO/CF<sub>x</sub> parallel cells, the low power CF<sub>x</sub> energy was converted to high power SVO energy. The utilization of CF<sub>x</sub> energy was also quantitative.

35

40 CONCLUSION

45 [0052] The above examples prove the feasibility of parallel discharging a high power cell, such as an SVO cell, with a high capacity cell, such as a CF<sub>x</sub>. By doing so, the energy of the high volumetric capacity CF<sub>x</sub> cell is quantitatively converted into or used as the high power energy of the SVO cell.

[0053] It is appreciated that various modifications to the inventive concepts described herein may be apparent to those skilled in the art without departing from the spirit and scope of the present invention defined by the hereinafter appended claims.

50

**Claims**

1. An electrochemical battery, comprising:

55 a. a first electrochemical cell comprising:

i. a first anode comprising alkali metal electrically associated with a first anode current collector;

- ii. a first cathode of a first cathode active material electrically associated with a first cathode current collector;
- iii. a first electrolyte operatively associated with the first anode and the first cathode; and

5        b. a second electrochemical cell comprising:

- i. a second anode comprising alkali metal electrically associated with a second anode current collector;
- ii. a second cathode of a second cathode active material electrically associated with a second cathode current collector;

10      iii. a second electrolyte operatively associated with the second anode and the second cathode; and

wherein the first cell is connected in parallel to the second cell and wherein the first cathode active material has a relatively high energy density but a relatively low rate capability and the second cathode active material has a relatively low energy density but a relatively high rate capability.

15      2. An electrochemical battery according to claim 1 wherein the first electrochemical cell comprises a terminal for connecting the first anode current collector to an external lead and a terminal for connecting the first cathode current collector to an external lead and the second electrochemical cell comprises a terminal for connecting the second anode current collector to an external lead and a terminal for connecting the second cathode current collector to an external lead.

20      3. An electrochemical battery according to claim 1 or claim 2 further comprising a casing in which said first electrochemical cell and said second electrochemical cell are housed.

25      4. An electrochemical battery according to any one of the preceding claims wherein the first and second cells are dischargeable under a substantially constant discharge rate and under a current pulse discharge application.

30      5. An electrochemical battery according to any one of the preceding claims wherein the first cell and the second cell are housed in the same casing and the first electrolyte and the second electrolyte are the same.

35      6. An electrochemical battery according to any one of the preceding claims wherein the first cathode active material is selected from the group consisting of  $CF_x$ ,  $Ag_2O$ ,  $Ag_2O_2$ ,  $CuF$ ,  $Ag_2CrO_4$ ,  $MnO_2$ , SVO, and mixtures thereof.

40      7. An electrochemical battery according to any one of the preceding claims wherein the second cathode active material is selected from the group consisting of SVO, CSVO,  $V_2O_5$ ,  $MnO_2$ ,  $LiCoO_2$ ,  $LiNiO_2$ ,  $LiMnO_2$ ,  $CuO_2$ , TiS,  $Cu_2S$ ,  $FeS_2$ , copper oxide, copper vanadium oxide, and mixtures thereof.

45      8. An electrochemical battery according to any one of claims 3 to 7 wherein the first and second anode current collectors are electrically connected to the casing to provide a case-negative configuration for the first and second cells.

50      9. An electrochemical battery according to any one of claims 3 to 7 wherein both the first and second cathode current collectors are electrically connected to respective cathode terminals electrically insulated from the casing.

55      10. An electrochemical battery according to any one of claims 3 to 7 wherein both the first and second anode current collectors are electrically connected to respective anode terminals electrically insulated from the casing.

11. An electrochemical battery according to any one of the preceding claims wherein the anode is comprised of lithium.

12. An electrochemical battery according to any one of the preceding claims wherein the anode comprises a lithium-aluminum alloy.

13. An electrochemical battery according to claim 12 wherein the aluminum comprises from between 0% to 50% by weight of the anode alloy.

14. An electrochemical battery according to any one of the preceding claims wherein the nonaqueous electrolyte comprises a first solvent selected from the group consisting of an ester, an ether, a dialkyl carbonate and mixtures thereof, and a second solvent selected from the group consisting of a cyclic carbonate, a cyclic ester, a cyclic

amide, and mixtures thereof.

15. An electrochemical battery according to any one of the preceding claims wherein the first solvent is selected from the group consisting of tetrahydrofuran, methyl acetate, diglyme, triglyme, tetraglyme, 1,2-dimethoxyethane, di-isopropylether, 1,2-diethoxyethane, 1-ethoxy, 2-methoxyethane, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, ethyl methyl carbonate, methyl propyl carbonate, ethyl propyl carbonate, and mixtures thereof.

16. An electrochemical battery according to any one of the preceding claims wherein the second solvent is selected from the group consisting of propylene carbonate, ethylene carbonate, butylene carbonate, acetonitrile, dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, Y-valerolactone, Y-butyrolactone, N-methyl-pyrrolidinone, and mixtures thereof.

17. An electrochemical battery according to any one of the preceding claims including providing an alkali metal salt in the electrolyte, the alkali metal salt being selected from the group consisting of LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiAsF<sub>6</sub>, LiSbF<sub>6</sub>, LiClO<sub>4</sub>, LiAlCl<sub>4</sub>, LiGaCl<sub>4</sub>, LiC(SO<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>, LiO<sub>2</sub>, LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>, LiSCN, LiO<sub>3</sub>SCF<sub>2</sub>CF<sub>3</sub>, LiC<sub>6</sub>F<sub>5</sub>SO<sub>3</sub>, LiO<sub>2</sub>CCF<sub>3</sub>, LiSO<sub>3</sub>F, LiB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, LiF<sub>3</sub>SO<sub>3</sub>, and mixtures thereof.

18. An electrochemical battery according to any one of the preceding claims wherein both the first and second cathodes comprise from between 80 weight percent to 99 weight percent of the respective first and second cathode active materials.

19. An electrochemical battery according to any one of the preceding claims wherein at least one of the first and second cathodes further comprises a binder material and conductive additives.

20. An electrochemical battery according to claim 19 wherein the binder material is a fluoro-resin powder.

21. An electrochemical battery according to claim 19 or claim 20 wherein the conductive additives are selected from the group consisting of carbon, graphite powder, acetylene black, and mixtures thereof.

22. An electrochemical battery according to any one of the preceding claims wherein the first and second cathodes comprise 0 to 3 weight percent carbon, 1 to 5 weight percent of a powder fluoro-resin and 94 to 99 weight percent of the respective first and second cathode active materials.

23. An electrochemical battery according to any one of the preceding claims wherein the cathode of the first cell is formed of a cathode sheet associated with the anode in a jellyroll configuration.

24. A method for providing an electrochemical battery according to any one of the preceding claims capable of discharge at both a substantially constant discharge rate and under a current pulse discharge application, which comprises:

a. providing a first electrochemical cell, comprising the steps of:

- i. providing a first anode comprising alkali metal and electrically associating the alkali metal with a first anode current collector;
- ii. providing a first cathode of cathode active material and electrically associating the first cathode active material with a first cathode current collector; and
- iii. activating the first electrochemical cell with an electrolyte solution operatively associated with the first anode and the first cathode; and

b. providing a second electrochemical cell, comprising the steps of:

- i. providing a second anode comprising alkali metal and electrically associating the alkali metal with a second anode current collector;
- ii. providing a second cathode of cathode active material and electrically associating the second cathode active material with a second cathode current collector; and
- iii. activating the second electrochemical cell with the electrolyte solution operatively associated with the second anode and the second cathode;

wherein the first cell is connected in parallel to the second cell and wherein the first cathode active material has a relatively high energy density but a relatively low rate capability and the second cathode active material has a relatively low energy density but a relatively high rate capability.

5    25. In combination with an implantable medical device requiring electrical power for a monitoring function and a device operating function, a battery comprising:

10    a. a first cell having a first anode comprising lithium and a first cathode comprising silver vanadium oxide;  
b. a second cell having a second anode comprising lithium and a second cathode comprising fluorinated carbon; and  
c. a casing containing both cells connected in parallel and activated by a nonaqueous electrolyte.

26. An electrochemical battery, which comprises:

15    a. a first cell having a first anode and a first cathode of a first cathode active material of a relatively high energy density but a relatively low rate capability;  
b. a second cell having a second anode and a second cathode of a second cathode active material of a relatively low energy density but a relatively high rate capability, wherein the first cell is connected in parallel to the second cell so that first and second cells are dischargeable together at a relatively low electrical current of about 1 microampere to about 100 milliamperes and wherein the second cell is dischargeable at a relatively high electrical current of about 1 to about 4 amperes such that should a background voltage of the second cell fall below a working voltage of the first cell, the second cell is recharged by the first cell to equalise each of their working voltages.

25    27. An electrochemical battery according to claim 26 wherein the first cell is of a Li/CF<sub>x</sub> couple.

28. An electrochemical battery according to claim 26 wherein the second cell is of a Li/SVO couple.

29. An electrochemical battery according to one of claims 26 to 28 powering a cardiac defibrillator.

30

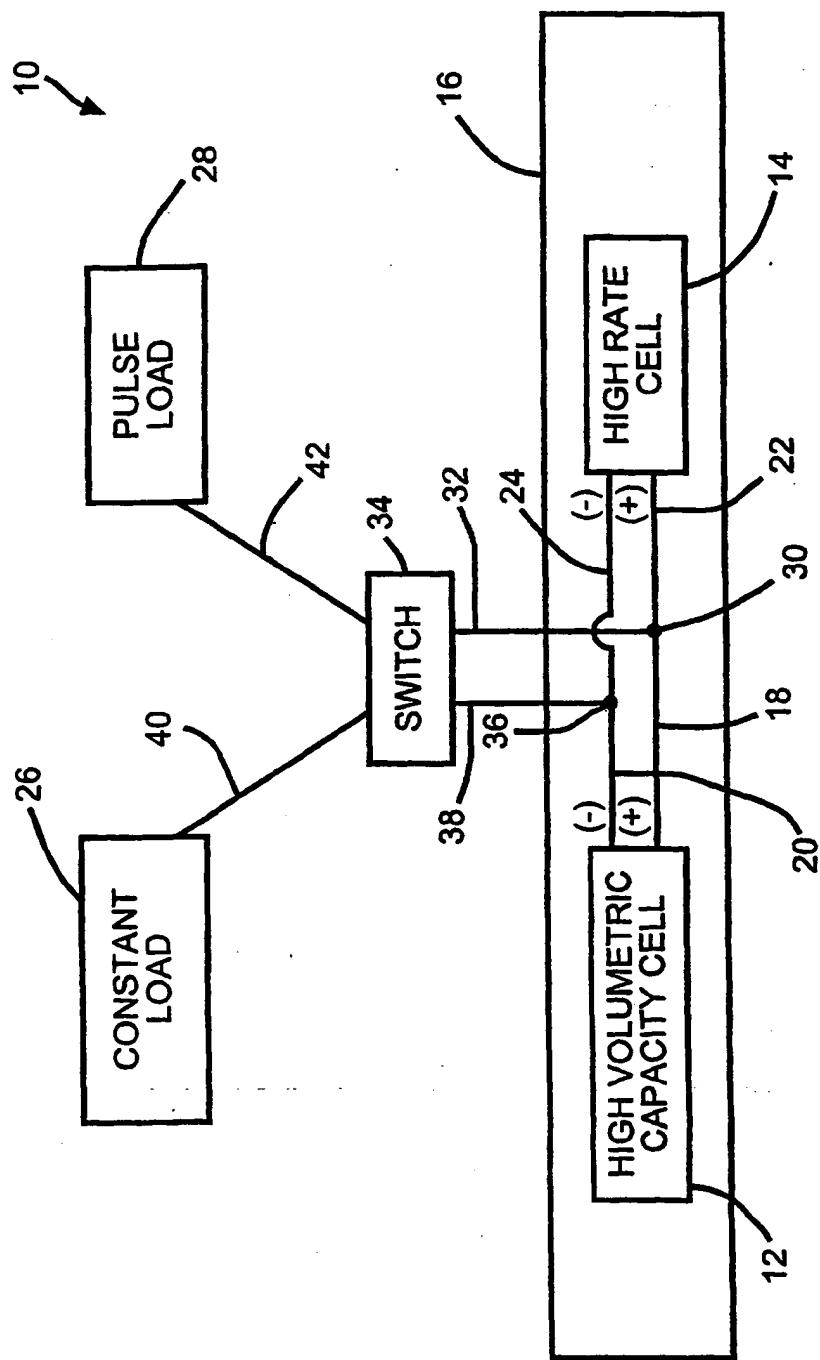
35

40

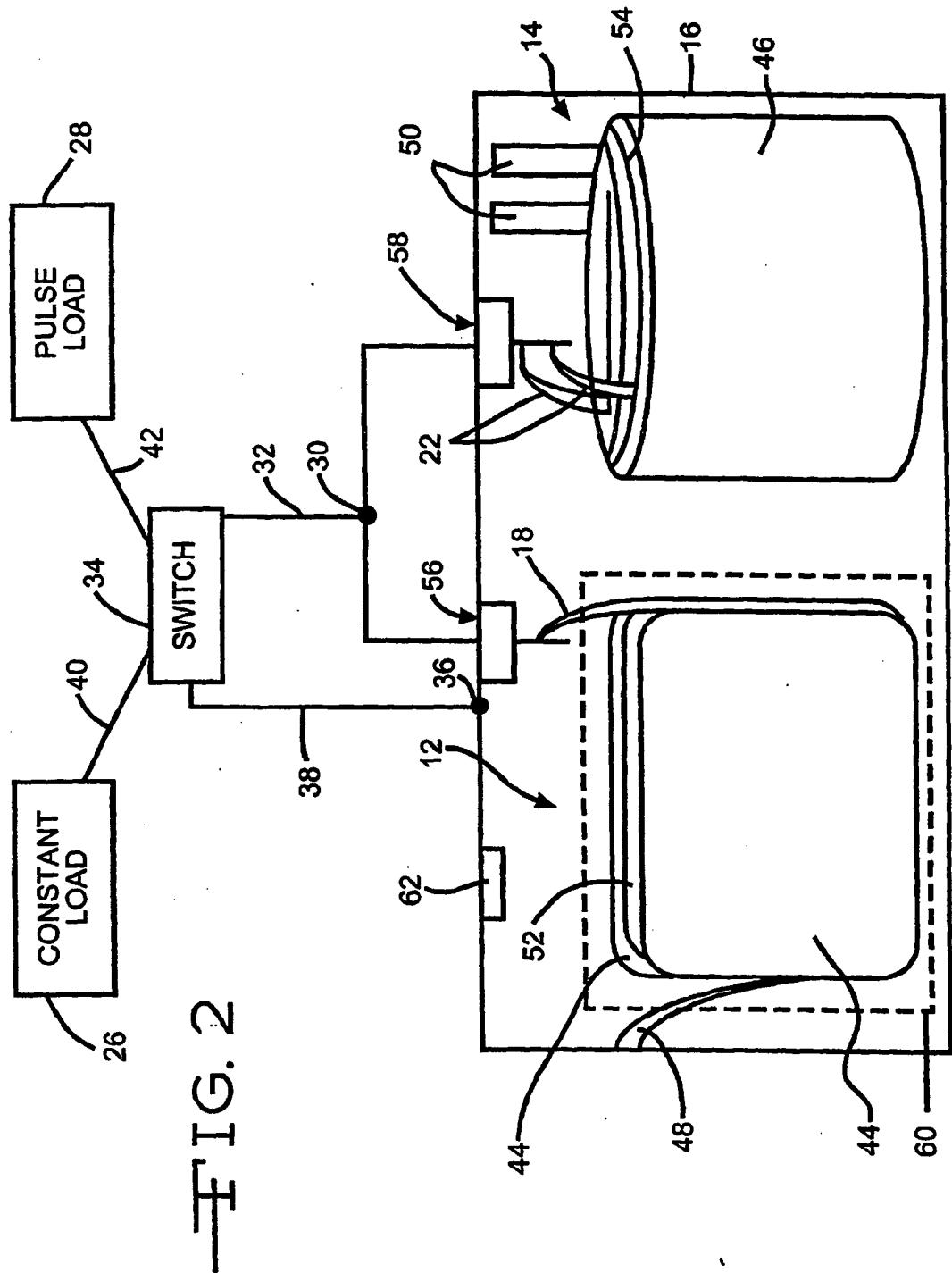
45

50

55



-FIG.1



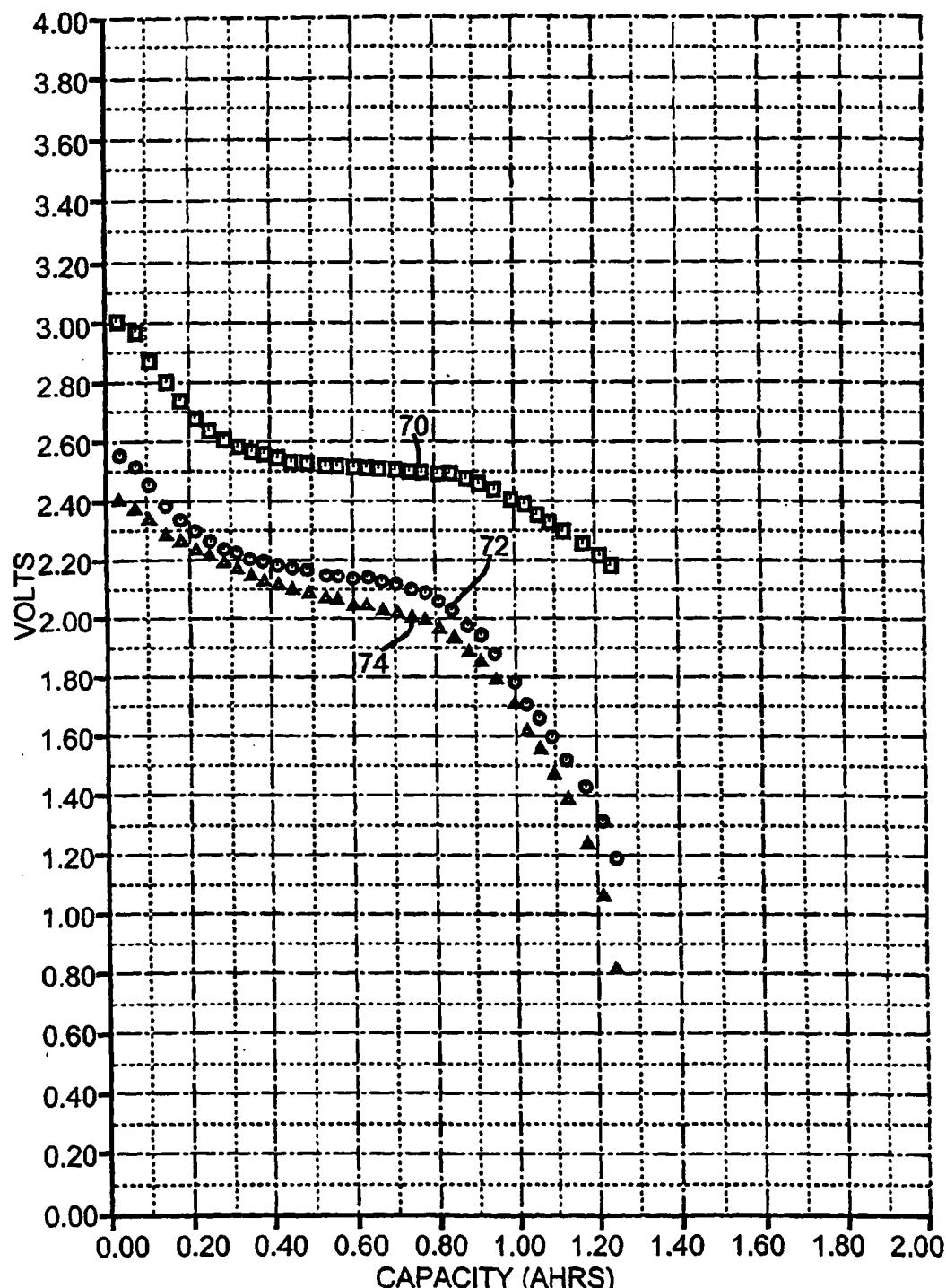


FIG. 3

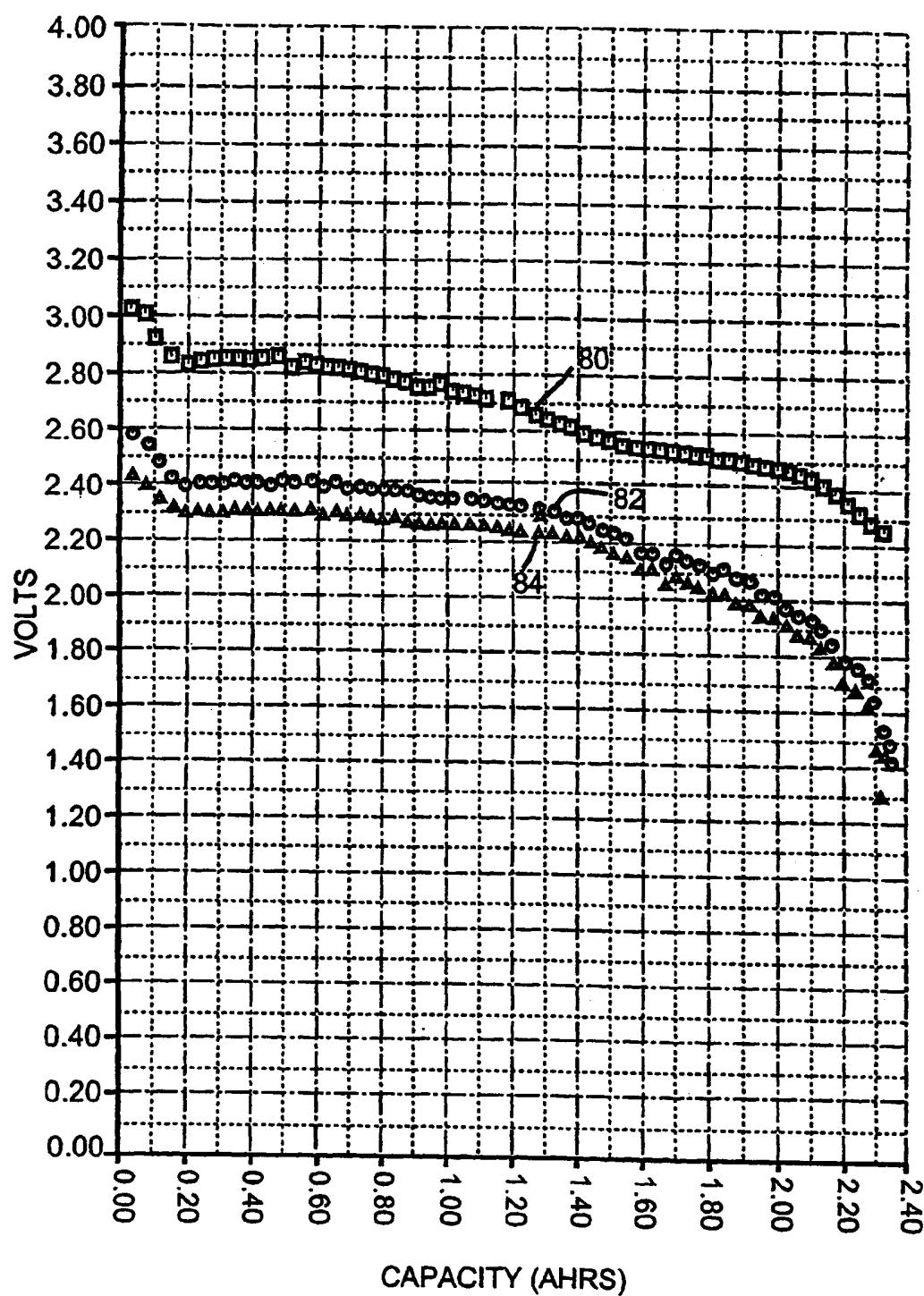


FIG. 4

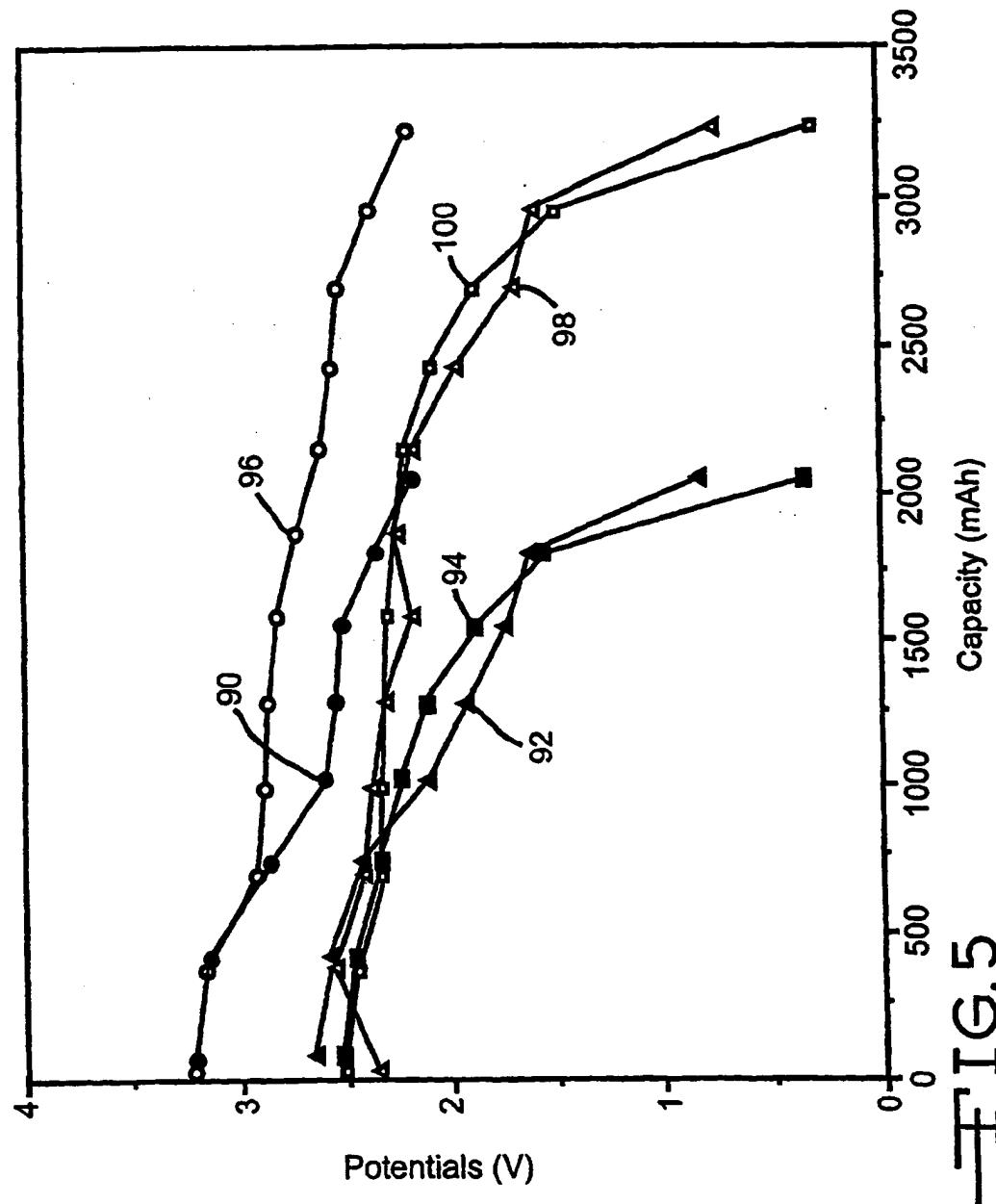


FIG. 5

This Page Blank (uspi0)



(19) Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 1 126 539 A3

(12)

## EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
18.09.2002 Bulletin 2002/38

(51) Int Cl.7: H01M 16/00, A61N 1/378,  
H02J 7/34, H01M 10/44

(43) Date of publication A2:  
22.08.2001 Bulletin 2001/34

(21) Application number: 01301379.2

(22) Date of filing: 16.02.2001

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 16.02.2000 US 183010 P

(71) Applicant: WILSON GREATBATCH LTD.  
Clarence New York 14031 (US)

(72) Inventors:  
• Gan, Hong  
East Amherst, New York 14051 (US)  
• Takeuchi, Esther S.  
East Amherst, New York 14051 (US)

(74) Representative: Bradley, Josephine Mary et al  
Mathys & Squire  
100 Gray's Inn Road  
London WC1X 8AL (GB)

### (54) Electrochemical battery for conversion of low rate energy into high rate energy by parallel discharging

(57) An electrode configuration for use in a defibrillator battery to improve the battery capacity and its utilization efficiency by using a combination SVO cell and a CF<sub>x</sub> cell discharged in parallel, is described. In other words, the anode of the SVO cell is connected to the

anode of the CF<sub>x</sub> cell and the cathode of the SVO cell is connected to the cathode of the CF<sub>x</sub> cell. The SVO cell provides a relatively high discharge rate while the CF<sub>x</sub> cell results in long service life. This results in 100% of the usable capacity from both cells being utilized.

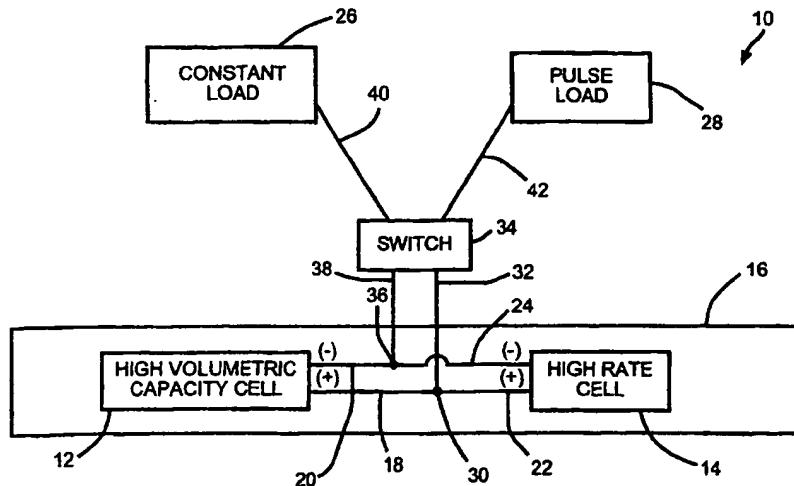


FIG.1

EP 1 126 539 A3



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 01 30 1379

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)
X	WO 99 28982 A (TADIRAN BATTERIES LTD ;YAMIN HERZEL (IL)) 10 June 1999 (1999-06-10) * page 3, line 2-20 * * page 6, line 3 - page 10, line 7 * * page 14, line 1 - page 15, line 9; claims 1-16 *	1,3,8,9, 11,23	H01M16/00 A61N1/378 H02J7/34 H01M10/44
X	US 2 594 988 A (FERNAND PORTAIL) 29 April 1952 (1952-04-29) * the whole document *	1,24	
A	US 4 134 408 A (BROWNLEE ROBERT R ET AL) 16 January 1979 (1979-01-16) * column 4, line 43 - column 5, line 45; claims 1-7 *	1,24	
A	US 5 814 075 A (KROLL MARK W) 29 September 1998 (1998-09-29) * column 3, line 11 - column 5, line 11; claims 1-24 *	1,4,6,7, 25-29	
A	GB 1 425 107 A (AMERICAN OPTICAL CORP) 18 February 1976 (1976-02-18) * the whole document *	1,24,25	TECHNICAL FIELDS SEARCHED (Int.Cl.) H01M A61N H02J
A	WO 99 05750 A (MAILE KEITH R ;WARREN JAY A (US); CARDIAC PACEMAKERS (US)) 4 February 1999 (1999-02-04) * page 2, line 14 - page 8, line 2; claims 1-21 *	1-4	
A	US 5 639 577 A (TAKEUCHI ESTHER S ET AL) 17 June 1997 (1997-06-17) * claims 1-55 *	1,5-7, 24,25	
		-/-	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search		Examiner
THE HAGUE	30 July 2002		De Vos, L
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons S : member of the same patent family, corresponding document	



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 01 30 1379

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 5 935 724 A (TAKEUCHI ESTHER S ET AL) 10 August 1999 (1999-08-10) * column 2, line 3-57 * * column 3, line 19 - column 6, line 50; claims 1,16-21,23,24 *	1,3,6-8, 11-22	
D,A	US 5 614 331 A (TAKEUCHI ESTHER S ET AL) 25 March 1997 (1997-03-25) * column 2, line 55 - column 8, line 11; claims 1-49 *	1-29	
-----			
TECHNICAL FIELDS SEARCHED (Int.Cl.7)			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	30 July 2002	De Vos, L	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 30 1379

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
 The members are as contained in the European Patent Office EDP file on  
 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

30-07-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 9928982	A	10-06-1999	US	5998052 A	07-12-1999
			AU	1172299 A	16-06-1999
			CA	2313016 A1	10-06-1999
			EP	1042827 A1	11-10-2000
			WO	9928982 A1	10-06-1999
			JP	2001525594 T	11-12-2001
US 2594988	A	29-04-1952	BE	492935 A	
			BE	517415 A	
			DE	834875 C	
			DE	945097 C	28-06-1956
			FR	1014165 A	20-08-1952
			GB	718947 A	24-11-1954
			GB	658361 A	10-10-1951
			NL	70630 C	
			NL	94751 C	
US 4134408	A	16-01-1979	NONE		
US 5814075	A	29-09-1998	NONE		
GB 1425107	A	18-02-1976	NONE		
WO 9905750	A	04-02-1999	EP	1004148 A1	31-05-2000
			WO	9905750 A1	04-02-1999
			US	6238813 B1	29-05-2001
US 5639577	A	17-06-1997	NONE		
US 5935724	A	10-08-1999	US	6258473 B1	10-07-2001
			US	2001038943 A1	08-11-2001
US 5614331	A	25-03-1997	AU	700923 B2	14-01-1999
			AU	7547496 A	26-06-1997
			DE	69602247 D1	02-06-1999
			DE	69602247 T2	23-09-1999
			EP	0780918 A1	25-06-1997
			JP	9199095 A	31-07-1997